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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention is excellent in antifoam, and relates to the developer for photoresists with wettability effective in the dissolution with good poor development.

[0002]

[Description of the Prior Art] In recent years, the densification of an integrated circuit is called for in semiconductor industry. Therefore, although the photoresist which has high resolution is used, an alkali fusibility photoresist like the photoresist which combined for example, the cresol novolak resin and the naphthoquinonediazide compound of a photolysis agent is used as one of them.

[0003]

[Problem(s) to be Solved by the Invention] As a developer at the time of using this kind of resist, although alkali solution is used, since alkali solution generally cannot fully be dipped to the base of a detailed pattern, the skirt piece of a base etc. becomes bad and it has the fault that a dimensional accuracy falls. Therefore, various kinds of surfactants are added in a certain kind of alkaline-water solution, and raising the wettability to a photoresist is proposed. However, when such a surfactant was used, there was a case where the bubble which was easy to foam and was produced did not disappear forever, but caused poor development.

[0004]

[Means for Solving the Problem] this invention is 1 water;

2) Alkali matter; and 3 (formula I):HO-B1-A-B2-H (I)

They are the compound which is shown by (A is a polypropylene-oxide machine among a formula, and B1 and B-2 are polyethylene-oxide machines) and with which average molecular weight is 900-4,000, and a polyethylene-oxide machine is contained five to 55% of the weight on the basis of average molecular weight, or formula (II):HO-A1-B-A2-H. (II) It is the developer for photoresists which is shown by (A1 and A2 are polypropylene-oxide machines among a formula, and B is a polyethylene-oxide machine) and which average molecular weight is 1,000-4,000, and contains the compound with which a polyethylene-oxide machine is contained five to 55% of the weight on the basis of average molecular weight.

[0005]

[Embodiments of the Invention] The water of what has higher purity used by this invention is better, and especially its ultrapure water is desirable.

[0006] Especially the alkali matter used by this invention is not limited. For example, a sodium hydroxide, a potassium hydroxide, a sodium silicate, a meta-sodium silicate, inorganic alkali; ammonia, such as sodium phosphate, phosphoric-acid hydrogen sodium, a sodium carbonate, and a sodium hydrogencarbonate; N propylamine, G n propylamine, G n butylamine, a methyl diethylamine, A collidine, a piperidine, a piperazine, a triethylenediamine, a pyrrole, Amines, such as 2 and 5-dimethyl pyrrole; A dimethylethanolamine, Alcoholic amines, such as a triethanolamine and a diethylhydroxylamine; the fourth class ammonium, such as tetramethylammonium hydroxide, tetraethylammonium hydroxide, and 2-hydroxyethyl trimethylammonium hydroxide, is mentioned. In this, tetramethylammonium hydroxide is desirable.

[0007] the addition of the alkali matter -- the water 100 weight section -- receiving -- desirable -- 0.1 - 5 weight section -- more -- desirable -- 0.2 - 4 weight section -- it is 0.5 - 3 weight section still more preferably

[0008] The compound of a formula (I) used by this invention is the hydrophilic polyethylene-oxide machine B1 about hydrophobic polypropylene-oxide machine A [the polymer machine which makes -CH(CH₃)CH₂O- a composition unit]. And B-2 It is the block copolymer sandwiched with [the polymer machine which makes -CH₂CH₂O- a composition unit], and is a nonionic surfactant.

[0009] Here, the average molecular weight of the compound of a formula (I) is 900-4,000, and the content of the polyethylene-oxide machine in this compound (B1 and B-2) is 5 - 55 % of the weight on the basis of the aforementioned average molecular weight. Preferably, the average molecular weight of the compound of a formula (I) is 900-2,200, and the content of the polyethylene-oxide machine in this compound is 5 - 35 % of the weight on the basis of the aforementioned average molecular weight. More preferably, the average molecular weight of the compound of a formula (I) is 900-2,200, and the content of the polyethylene-oxide machine in this compound is 5 - 15 % of the weight on the basis of the aforementioned average molecular weight. Most preferably, the average molecular weight of the compound of a formula (I) is 900-1,200, and the content of the polyethylene-oxide machine in this compound is 5 - 15 % of the weight on the basis of the aforementioned average molecular weight.

weight. In addition, B1 And B-2 It is B1 that a total content should just be within the limits of the above. B-2 Each may have what average molecular weight.

[0010] As a compound of a formula (I) used by this invention For example, PLURONIC (Registered trademark) L31, L35, L42, L43, L44, L61, L62, L63, L64, L72, L81, L92, L101, L121, L122, P65, P75, P84, P85, P103, P104, P105, P123 of series (above) The BASF A.G. make etc. is mentioned. The content (% of the weight) of the polyethylene-oxide machine on the basis of such average molecular weight and average molecular weight is shown in Table 1.

[0011]

[Table 1]

式 (I) の化合物	平均分子量	ポリエチレンオキシド 基の含有量 (重量%)
L31	1,100	10
L35	1,900	50
L42	1,630	20
L43	1,850	30
L44	2,200	40
L61	2,000	10
L62	2,500	20
L63	2,650	30
L64	2,900	40
P65	3,400	50
L72	2,750	20
P75	4,150	50
L81	2,750	10
P84	4,200	40
P85	4,600	50
L92	3,650	20
L101	3,800	10
P103	4,950	30
P104	5,900	40
P105	6,500	50
L121	4,400	10
L122	5,000	20
P123	5,750	30

[0012] Moreover, the compound of a formula (II) used by this invention is the hydrophobic polypropylene-oxide machine A1 about polyethylene-oxide machine [of a hydrophilic property] B [the polymer machine which makes -CH₂ CH₂ O- a composition unit]. And A2 It is the block copolymer sandwiched with [the polymer machine which makes -CH(CH₃) CH₂ O- a composition unit], and is a nonionic surfactant.

[0013] Here, the average molecular weight of the compound of a formula (II) is 1,000-4,000, and the content of the polyethylene-oxide machine in this compound (B) is 5 - 55 % of the weight on the basis of the aforementioned average molecular weight. Preferably, the average molecular weight of the compound of a formula (II) is 1,000-4,000, and the content of the polyethylene-oxide machine in this compound is 15 - 45 % of the weight on the basis of the aforementioned average molecular weight. Moreover, preferably, the average molecular weight of the compound of a formula (II) is 1,000-2,900, and the content of the polyethylene-oxide machine in this compound is 5 - 55 % of the weight on the basis of the aforementioned average molecular weight. More preferably, the average molecular weight of the compound of a formula (II) is 2,000-2,900, and the content of the polyethylene-oxide machine in this compound is 15 - 45 % of the weight on the basis of the aforementioned average molecular weight. In addition, A1 And A2 It is A1 that a total content should just be within the limits of the above. A2 Each may have what average molecular weight.

[0014] As a compound of a formula (II) used by this invention, ten R5 of PLURONIC(registered trademark) R series, 12R3, 17R1, 17R2, 17R4, 22R4, 25R1, 25R2, 25R4, 25R5, 31R1, 31R2, 31R4 (above, BASF A.G. make), etc. are mentioned, for example. The content (% of the weight) of the polyethylene-oxide machine on the basis of such average molecular weight and average molecular weight is shown in Table 2.

[0015]

[Table 2]

式 (II) の化合物	平均分子量	ポリエチレンオキシド 基の含有量 (重量%)
10R5	1,950	50
12R3	1,800	30
17R1	1,900	10
17R2	2,150	20
17R4	2,650	40
22R4	3,350	40
25R1	2,700	10
25R2	3,100	20
25R4	3,600	40
25R5	4,250	50
31R1	3,250	10
31R2	3,300	20
31R4	4,150	40

[0016] The developer for photoresists of this invention is 50-5,000 ppm preferably about the compound of the above (I) or (II) on the basis of the weight of water and the alkali matter. It contains and is 50-500 ppm still more preferably 50-1,000 ppm more preferably. It contains.

[0017] In addition, the "average molecular weight" said to this specification means what was computed based on the hydroxyl value measured according to the following procedure (FUTARU-ized method).

[0018] The pyridine solution of the reagent ** phthalic anhydride to be used: Dissolve 42g of phthalic anhydride in pyridine 300ml completely, and ripen one night at 2 hours or a room temperature by 70 degrees C. In addition, this reagent is saved in a colored bottle and what was updated and colored within eight days does not use it.

** The pyridine solution of a pyridine ** 0.5-N sodium-hydroxide solution ** phenolphthalein (1w/v %)

[0019] The sample of the amount of procedure ** conventions is correctly measured in 300ml flask [S (g)]. In addition, when output is less than 1g, it is 10-1mg order, and when output is 1g or more, it measures to mg order.

** In addition, heat at a transfer pipet for 2 hours on the water bath boiled after carrying out the seal of the ***** by the pyridine correctly [25ml of pyridine solutions of phthalic anhydride] (it shakes and moves every 15 minutes).

** After heating, take out from a water bath and cool to ordinary temperature.

** ** -- flush a plug by the pyridine (a penetrant remover is dropped into a flask), and add 0.5-N sodium-hydroxide solution correctly with 50ml transfer pipet

** Add ten drops of indicators (pyridine solution of a phenolphthalein).

** Titrate with 0.5-N sodium-hydroxide solution [A (ml)]. The point which maintains red for at least 15 seconds is made into a terminal point.

** This examination performs a blank test on the same conditions [B (ml)].

[0020] The amount of 0.5-N sodium-hydroxide solutions (ml) which the hydroxyl value (mgKOH/g) took OHV to among the calculation $OHV = [28.05 \times (B-A) \times f] / S$ formula of the calculation ** hydroxyl value of average molecular weight, and the titration of a blank test took B, the amount of 0.5-N sodium-hydroxide solutions (ml) which the titration of a sample took A, and f show the factor of 0.5-N sodium-hydroxide solution, and S shows the amount of samples (g). In addition, when a sample contains a free acid, it amends by the following formula.

Calculation average molecular weight of correction value = hydroxyl value + acid-number ** average molecular weight = $(56.1 \times 2 \times 1000)$ as for 56.1, the formula weight of KOH and 2 are the number of functional groups (OH basis) among a /OHV formula.

[0021]

[Example]

The 0.005 weight section dissolution of the PLURONIC-10R5 by BASF A.G. which are equivalent to the compound of a formula (II) at the 2.38% trimethylammonium hydroxide solution 100 weight section of manufactures of example 1 developer is carried out, and it is 50 ppm about the aforementioned compound. The included developer for photoresists was manufactured.

[0022] The positive-type photoresist SRR 6809 (SHIPUREI Far East company make) was applied to the 4 inches silicon wafer of wettability examinations so that it might become 0.9 micrometers of thickness, and the prebake was carried out to it for 45 seconds at 105 degrees C among clean oven. In order to drop the above-mentioned developer at this wafer and to grasp the grade which gets wet, the contact angle of a developer was measured with the contact angle plan. Consequently, the value of 55.2 degrees was acquired.

[0023] The 25ml of the antifoam test above-mentioned developers was dropped at 50ml measuring cylinder of glass from a height of 50cm for the glass transfer pipet. And the height of the bubble immediately after a dropping end and the height of the bubble of 5 minutes after were measured. In addition, the above-mentioned examination was performed at 25 degrees C. Consequently, although the height of the bubble immediately after a dropping end was 3mm, after 5 minutes, defoaming of it was carried out completely.

[0024] Except having changed the kind and concentration of one to examples 2-12 and example of comparison 3 surfactant, as shown in Table 1, it got wet in the same procedure as an example 1, and the sex test and the antifoam examination were

performed. The result is shown in Table 1. As shown in Table 1, the developer concerning this invention had the contact angle smaller than the conventional developer, and, moreover, carried out defoaming after 5 minutes in all the examples. Therefore, the developer concerning this invention excels the conventional developer in wettability and antifoam.

[0025]

[Table 3]

	有機塩基		界面活性剤		接触角(°)	泡高さ(mm)	
	種類	濃度(重量%)	種類	濃度(ppm)		調下直後	5分後
比較例1	TMAH	2.38	なし		65.4	0	0
比較例2	"	2.38	サーフィノール46S*1	50	60.3	8	2
比較例3	"	2.38	PLURONIC F68*2	500	60.3	10	7
実施例1	"	2.38	PLURONIC R 10R5	50	55.2	3	0
実施例2	"	2.38	"	250	54		
実施例3	"	2.38	"	1000	51		
実施例4	"	2.38	PLURONIC R 17R2	50	53.4	3	0
実施例5	"	2.38	"	250	47.5		
実施例6	"	2.38	"	1000	42.9		
実施例7	"	2.38	PLURONIC R 17R4	50	55.9	3	0
実施例8	"	2.38	"	250	50.8		
実施例9	"	2.38	"	1000	47.5		
実施例10	"	2.38	PLURONIC L31	50	54.5	5	0
実施例11	"	2.38	"	250	51.5		
実施例12	"	2.38	"	1000	49		

*1 エアプロダクツアンドケミカルズ社、アセチレンアルコール系界面活性剤

*2 式(1)の化合物(平均分子量=8,400、ポリエチレンオキシド基含有量=80重量%)

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CLAIMS

[Claim(s)]

[Claim 1] 1) Water;

2) Alkali matter; and 3 (formula I):HO-B1-A-B2-H (I)

They are the compound which is shown by (A is a polypropylene-oxide machine among a formula, and B1 and B-2 are polyethylene-oxide machines) and with which average molecular weight is 900-4,000, and a polyethylene-oxide machine is contained five to 55% of the weight on the basis of average molecular weight, or formula (II):HO-A1-B-A2-H. (II)

It is the developer for photoresists characterized by containing the compound which is shown by (A1 and A2 are polypropylene-oxide machines among a formula, and B is a polyethylene-oxide machine), and with which average molecular weight is 1,000-4,000, and a polyethylene-oxide machine is contained five to 55% of the weight on the basis of average molecular weight.

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(19)



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HIDANO MANABU
AWAJI AKIRA**(54) **DEVELOPER FOR PHOTORESIST**

(57) Abstract:

PROBLEM TO BE SOLVED: To obtain a developer for a photoresist excellent in defoamability, having satisfactory wetting property and effective to prevent defective development by incorporating water, an alkali material and a compd. contg. specified polyethylene oxide groups.

SOLUTION: This developer contains water, an alkali material and a compd. represented by the formula HO-B_1 -A-B₂-H, having an average mol.wt. of 900-4,000 and contg. 5-55 wt.% polyethylene oxide groups based on the average mol.wt. In the formula, A is a polypropylene oxide group and B₁ and B₂ are polyethylene oxide groups. The compd. represented by the formula is a block copolymer obtd. by sandwiching a hydrophobic polypropylene oxide group A which is a polymer group contg. $-\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-$ as constituent units between hydrophilic polyethylene oxide

groups B₁ and B₂ which are polymer groups each contg. $-\text{CH}_2\text{CH}_2\text{O}-$ as constituent units and it is a nonionic surfactant. This developer is excellent in defoamability, has satisfactory wetting property and prevents defective development.

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